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14. ABSTRACT Amorphous (La _x Al _{1-x}) ₂ O ₃ (0.61 less than or equal to x less than or equal 0.73) films have been deposited by sputtering in a partially reactive atmosphere. The average dielectric constant of the as-deposited films was 13.4 and 12.5 following annealing at 700°C for 60 min in N ₂ ; both values were much lower than the single crystal values ~24 and 28 for LaAlO ₃ and La ₂ O ₃ , respectively. Leakage current densities were ~10 ⁻⁸ A cm ⁻² for an applied field of 1 MV cm ⁻¹ for film thicknesses ~75 nm. Fourier transform infrared spectroscopy reveals transverse optic mode peaks at 723 and 400 cm ⁻¹ and corresponding longitudinal optic modes at 821 and 509 cm ⁻¹ . The density of the amorphous phase is estimated to be ~0.9 times the crystalline density.					
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Infrared and electrical properties of amorphous sputtered $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ films

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Amorphous $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ ($0.61 \leq x \leq 0.73$) films have been deposited by sputtering in a partially reactive atmosphere. The average dielectric constant of the as-deposited films was 13.4 and 12.5 following annealing at 700 °C for 60 min in N_2 ; both values were much lower than the single crystal values ~ 24 and 28 for LaAlO_3 and La_2O_3 , respectively. Leakage current densities were $\sim 10^{-8} \text{ A cm}^{-2}$ for an applied field of 1 MV cm^{-1} for film thicknesses $\sim 75 \text{ nm}$. Fourier transform infrared spectroscopy reveals transverse optic mode peaks at 723 and 400 cm^{-1} and corresponding longitudinal optic modes at 821 and 509 cm^{-1} . The density of the amorphous phase is estimated to be ~ 0.9 times the crystalline density. © 2003 American Institute of Physics.

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I. INTRODUCTION

A variety of criteria must be satisfied when choosing an alternative dielectric to replace SiO_2 in memory cell applications or as gate oxides in metal–oxide–semiconductor field-effect transistors (MOSFETs). The extent of the criteria, such as band offsets,¹ thermodynamic stability with the silicon substrate,² dielectric/Si interface quality, etc., is unquestionably the reason why dielectrics with a modest permittivity ~ 12 have emerged as medium term candidates.³ In essence, the solution adopted appears to be one of using a silicate base in which a high dielectric constant material is diluted, for example HfO_2 ($k \sim 22$) in SiO_2 ($k \sim 3.9$). The presence of the SiO_2 intuitively improves the compatibility of the dielectric with the Si substrate and, furthermore, renders the resultant ternary oxide amorphous up to a very high temperature which is a desirable feature since grain-boundary leakage currents frequently arise in polycrystalline films. Nitridation of the silicate films ($\text{Hf}_x\text{Si}_y\text{O}_{2-z}\text{N}_z$) further stabilizes the amorphous phase⁴ and improves the resistance to B diffusion which is important if B-doped Si is used in the gate electrode, for example.

The Hf silicate solution will undoubtedly resolve the need of technology for an alternative MOSFET gate dielectric for a limited number of generations of devices. In the longer term, a higher dielectric constant material (say $k \sim 22$) may be desirable. As a general rule,¹ the dielectric constant is inversely proportional to the electronic band gap so that band offset effects become significant and many high dielectric constant materials must be excluded because the barrier height to carrier injection from the Si conduction/valence bands to the insulator conduction/valence bands is too small. Ta_2O_5 is an excellent example.¹ Two materials

which have acceptable dielectric constants, adequate band gaps,⁵ and band offsets¹ are LaAlO_3 ($k \sim 24$) and La_2O_3 ($k \sim 28$). Furthermore, both are predicted² to be thermodynamically compatible with Si. Note, however, that La_2O_3 is moisture sensitive so it may not be suitable in a microelectronics processing environment. In the work reported here, the author has begun a study of the electrical and physical properties of $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ ($x \geq 0.61$) deposited by sputtering of an LaAlO_3 target in a partially reactive atmosphere.

II. EXPERIMENT

n- or *p*-type Si (100) 3–5 ohm cm resistivity wafers were first rinsed in HF acid then blown dry. Thin $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ films were deposited at room temperature by sputtering from a polycrystalline LaAlO_3 target using a 13.56 MHz radio frequency (rf) sputtering source (TORUS 2) with an Ar/ O_2 gas mixture. The chamber pressure was 10 mTorr and the gas flow rates were 75 sccm for Ar and 5 sccm for O_2 . The typical rf power was 80 W. Assistance in exciting the plasma and increasing its density was provided via a six-antenna microwave excited electron cyclotron resonance structure; here, the frequency was 2.45 GHz and the power typically 400 W. Finally, the substrate holder and sample were biased using a 13.56 MHz rf source; a power of 40 W resulted in a substrate potential of -90 V . This bias was used to provide some ion assisted deposition of the film and so densifies it. Under these conditions, $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ films were obtained with $0.61 \leq x \leq 0.73$ as determined by x-ray photoelectron spectroscopy (XPS) profiling. The rate of deposition of the film was typically 1.4 nm min^{-1} . Typical film thicknesses were between 70 nm and 100 nm. A second set of samples whose stoichiometry was not ascertained was produced by electron-beam (e-beam) evaporation using bulk LaAlO_3 wafers as the evaporation source. The base pressure in the chamber was $1.0 \times 10^{-6} \text{ Torr}$ and, during evaporation, an

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oxygen pressure of 1.0×10^{-4} Torr was used. The film thickness and refractive index (n) for all films were determined using single wavelength (632.8 nm) ellipsometry; the film thickness was also confirmed by measurement of the Kissig fringes obtained using small angle x-ray reflectivity. Metal-oxide-semiconductor capacitor structures were manufactured using a shadow mask to define Al dots produced by thermal evaporation. The back face of the wafers was also metallized to ensure electrical contact. Capacitance-voltage (C - V) curves were measured at a frequency of 100 kHz using a Keithley 590 system. The same system was used to measure leakage current density (J) as a function of applied voltage (V). Prior to electrode deposition, wafers were cleaved and some samples were subjected to an anneal at 700 °C for between 10 and 60 min in N_2 . A set of samples without Al dots or back face metallization was used for the x-ray reflectivity studies and for Fourier transform infrared (FTIR) absorption measurements, some of these samples were annealed up to 900 °C in N_2 for 30 min.

III. RESULTS

The primary objective of the experiments reported here was not to study in any detail the e-beam evaporated material, but to use it as a reference. Other authors have studied the properties of e-beam evaporated $LaAlO_3$ films,⁶ and their films were found to be amorphous even after annealing at 700 °C for 10 min in N_2 . The C - V and current-voltage (I - V) data reported indicated dielectric constants ~ 24 and current densities of the order of $10^{-5} \text{ A cm}^{-2}$ for an electric field $\sim 1 \text{ MV cm}^{-1}$ in annealed samples. These data were not reproducible in the e-beam evaporated material. Although current densities $\sim 10^{-5} \text{ A cm}^{-2}$ were observed for an electric field of $\pm 1 \text{ MV cm}^{-1}$ in unannealed 80 nm thick samples, 700 °C anneals for 10 min in N_2 severely degraded the I - V characteristic. Furthermore, unannealed samples revealed dielectric constants of only ~ 7.5 and refractive indices of 1.632 at 632.8 nm; following annealing, the dielectric constant rose to ~ 11 and the refractive index increased to 1.68. The author has no explanation for the discrepancy between these data and the previous authors'.⁶

In Fig. 1, we show typical C - V and current density-electric field (J - E) data for $(La_xAl_{1-x})_2O_3$ samples deposited by sputtering then annealed for 30 min in N_2 at 700 °C, the substrate was p type. E is simply assumed to be the applied voltage divided by the film thickness. The film thickness for this example was 75.4 nm as determined ellipsometrically. From XPS measurements, we determined $x \sim 0.61$. Prior to annealing, we obtained an average dielectric constant of ~ 11 and a refractive index of 1.77 while these values changed to 12.5 and 1.82, respectively, following annealing at 700 °C in N_2 for 60 min. For other samples with $x = 0.73$, we obtained $k \sim 13.4$ ($n \sim 1.75$) before anneal and $k \sim 12.5$ ($n \sim 1.78$) following 60 min in N_2 at 700 °C. We were unable to obtain samples having a dielectric constant exceeding 13.4.

Assuming an Al electrode and a substrate with the doping level $\sim 10^{15} \text{ ions cm}^{-3}$ as we have used, the metal/semiconductor work function difference is approximately

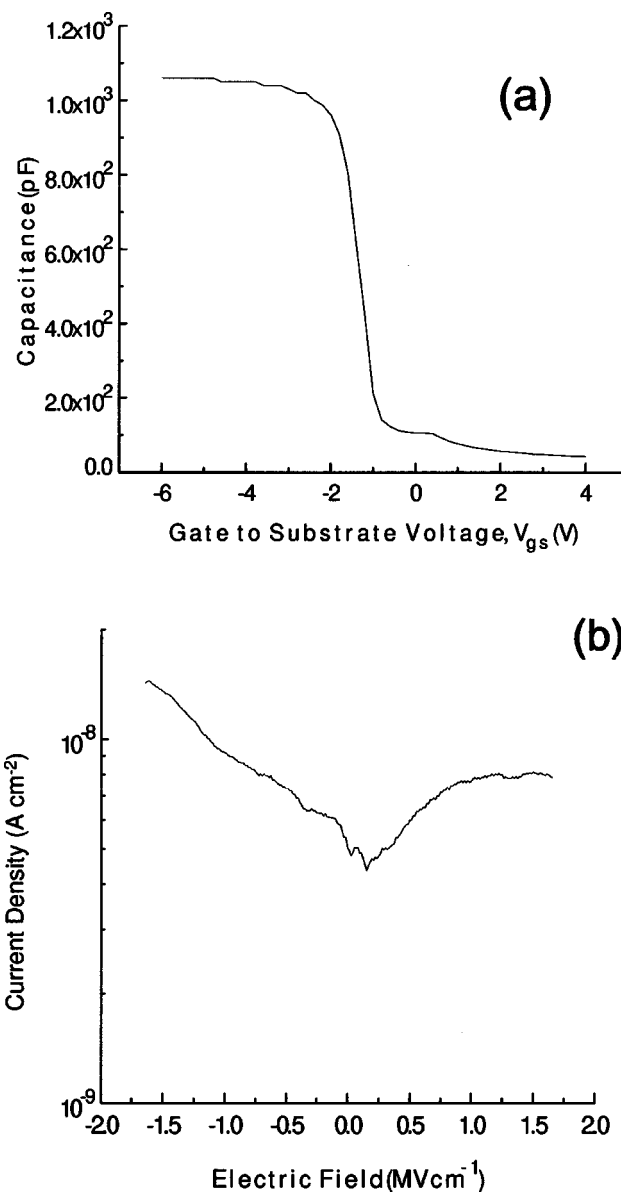


FIG. 1. (a) C - V curve measured at 100 kHz in a sputter deposited sample annealed at 700 °C for 30 min in N_2 . (b) Current density as a function of applied electric field measured on the same sample.

~ 0.9 V so that, in the absence of interface state and trapped oxide charge effects, we would expect a flat-band voltage of this magnitude.⁷ The C - V curve shown in Fig. 1 is consistent with a flat-band voltage in the -1 to -2 V region suggesting that trapped charge and interface state effects are not dramatic. Repeated cycling of the C - V curve evidenced little or no hysteresis at first sight. However, bias stressing followed by rapid C - V measurement indicated the possible presence of mobile, positive charges in both the as-deposited and annealed films. These measurements will not be addressed here since we are primarily concerned with measurements of the dielectric constant.

In Fig. 2, we show the results of FTIR absorption spectroscopy measurements on annealed sputtered films. The samples studied were cleaved from the same wafers as used for the C - V and J - V measurements. The absorption spectrum observed for an unannealed film is identical to that

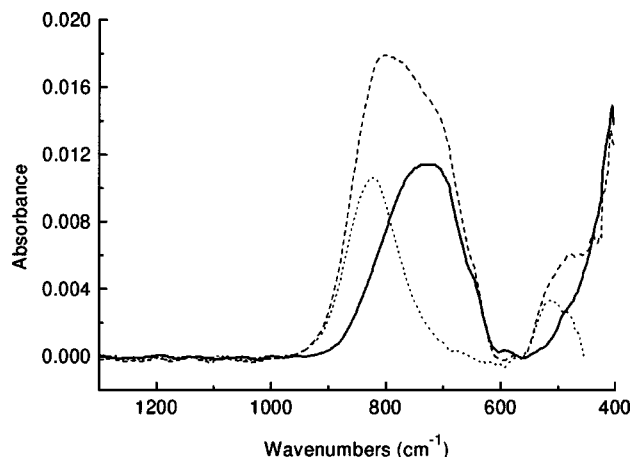


FIG. 2. FTIR spectra in samples of $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ obtained by sputtering then annealing at 700°C for 30 min in N_2 . The solid line corresponds to the normal incidence spectrum (TO modes), the dashed line is the combined TO and LO mode spectrum obtained at an angle of incidence of 65° and the dotted line is the LO mode spectrum obtained by subtracting the TO spectrum from the mixed mode spectrum.

found for the 700°C annealed film consistent with the film being amorphous even after annealing at that temperature. One curve corresponds to the normal incidence beam spectrum while another corresponds to the spectrum observed for an angle of incidence of 65° . Under non-normal incidence conditions both transverse optic (TO) and longitudinal optic (LO) vibrational modes are excited in the film.⁸ We note that no absorption is seen in the region of $1050\text{--}1100\text{ cm}^{-1}$ in the normal incidence spectrum or at 1250 cm^{-1} in the 65° incidence spectrum. Since this is the “classical” region for strong vibrational modes in SiO_2 , we can conclude that there is a negligible amount of SiO_2 present in the structure—in particular, at the $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3/\text{Si}$ substrate interface. We can, therefore, reasonably suggest that the low dielectric constant we have measured in the amorphous $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ films does not result from the presence of an interfacial SiO_2 film which would reduce the overall dielectric constant. Consequently, the low dielectric constant is intrinsic to the nature of the deposited amorphous film. Also shown in Fig. 2 is the curve resulting from the subtraction of the normal incidence data from the 65° incidence spectrum. The spectrum is indicative of the pure LO modes and this allows one to ascertain that the amorphous film peaks occur at approximately 821 and 509 cm^{-1} . The pure TO mode peaks occur at 723 and 400 cm^{-1} , respectively, although little precision can be attributed to the latter value since the complete peak shape with its maximum is not resolved. In Fig. 3, we show the normal incidence FTIR spectrum for a sputtered film annealed for 30 min in N_2 at 900°C . We include the 700°C annealed spectrum for comparison. The higher-temperature annealing has clearly transformed the film and an intense peak centered upon 912 cm^{-1} has appeared. This peak position is rather similar to that observed⁹ in the annealing of La_2O_3 films on Si which is attributed to O vibrations in Si–O–La linkages. It clearly suggests that 900°C annealing of $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ on Si results in an interaction of the Si

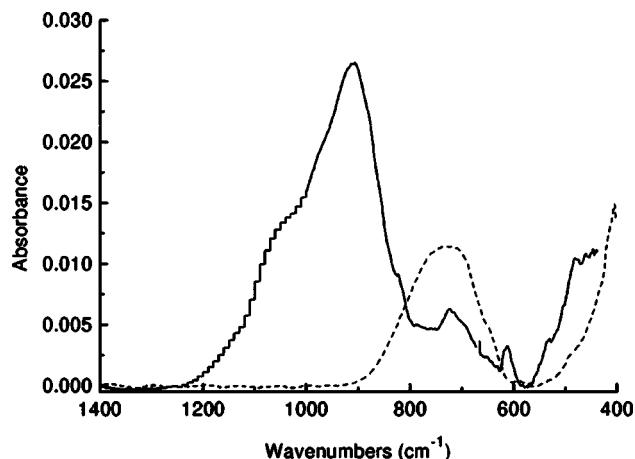


FIG. 3. Normal incidence FTIR spectra for a $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ sample deposited by sputtering then annealed at 700°C for 30 min in N_2 (dashed line) or 900°C for 30 min in N_2 (solid line). In the latter case, one observes a strong peak around 912 cm^{-1} which may be due to Si–O–La linkages and a peak around 1050 cm^{-1} due to Si–O–Si linkages. There has clearly been a reaction between the deposited film and the Si substrate.

with the film. This is not anticipated on the basis of thermodynamic calculations of phase stability.²

IV. DISCUSSION

In Fig. 4, we schematically show the dielectric constant as a function of x in $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ compounds. We include a point for Pr_2O_3 which is characteristic of most of the lanthanide sesquioxides, i.e., $k \sim 14$. The x values for the samples we have prepared would suggest that they should have dielectric constants lying somewhere between the known LaAlO_3 and La_2O_3 values. It would appear that the data we have obtained in fact lies reasonably on an interpolation between Al_2O_3 and Pr_2O_3 while the crystalline phase lanthanide values (LaAlO_3 and La_2O_3) are significantly

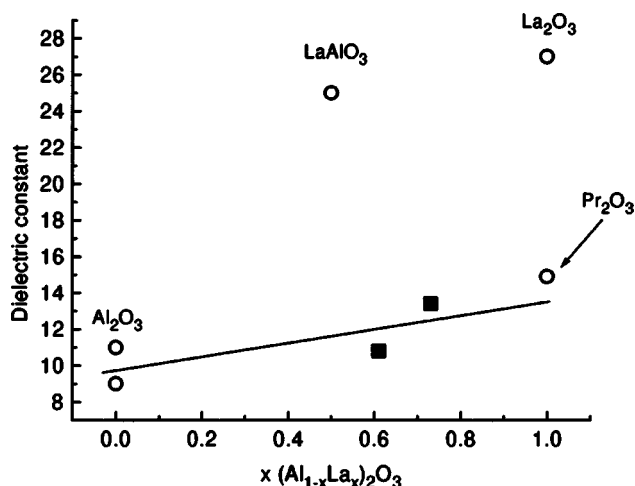


FIG. 4. A plot of the dielectric constant as a function of x in amorphous and crystalline $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ compounds, the value for Pr_2O_3 is included since it is typical of most lanthanide sesquioxides. La_2O_3 is unusually large due primarily to larger molar polarizability.

higher. We must, therefore, address the issue of the discrepancy in dielectric constants between the deposited amorphous materials and crystalline forms.

In order to give further credibility to the values of a dielectric constant that we have measured, we can appeal to the infrared absorption data. The low- $[k(0)]$ and high- $[k(\infty)]$ frequency dielectric constants are related to the TO and LO vibrational frequencies through the Lyddane–Sachs–Teller relationship.¹⁰ When various modes of vibration are present, this may be written:¹¹

$$k(0)/k(\infty) = \prod_j \omega_j^2 \text{LO} / \omega_j^2 \text{TO}, \quad (1)$$

where the product is over all vibrational modes ω_j . We assume that the high-frequency dielectric constant is given by $k(\infty) = n^2$, where n is the refractive index. For the crystalline phase of LaAlO_3 , the TO and LO vibrational mode frequencies have been calculated¹² and, using the refractive index value¹³ of 2.04 in Eq. (1), we ascertain $k(0) = 29$ which is close to the measured value¹⁴ ~ 24 . If we use the TO and LO vibrational frequencies, we have measured for the amorphous $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ films together with the refractive index measured at 632.8 nm, we deduce $k(0) = 6.92$. This value is significantly lower than the value we have measured of 13.4, but it has the merit that it is closer to the experimental amorphous dielectric constant than that expected for crystalline material (assuming that for the samples we have studied with $x \geq 0.61$, the dielectric constant of a crystalline material would lie between LaAlO_3 and La_2O_3 values). It is also possible that there are vibrational modes and splittings that we have not included in the calculation based upon Eq. (1) (for frequencies less than 400 cm^{-1}) and this needs to be further explored using an FTIR capable of measuring at lower wave numbers.

The experimental value of $k(0) = 13.4$ for $(\text{La}_{0.73}\text{Al}_{0.27})_2\text{O}_3$ remains, then, becomes considerably lower than the crystalline values of 24 for LaAlO_3 or 28 for La_2O_3 . Could one explanation be that the deposited films are porous? We note first that ion beam assistance (sample bias) was used during deposition and, that secondly, the effects of annealing on the dielectric constant were rather small suggesting that the film had reached some limiting dielectric constant value. Independent confirmation of the correct value is required.

In the simplest interpretation of the dielectric constant, it may be determined through the Clausius Mossotti equation:¹⁰

$$(k-1)/(k+2) = (4\pi/3)\alpha/V_m, \quad (2)$$

where V_m is the molecular volume and α the molecular polarizability. For the crystalline phases, we obtain $\alpha/V_m = 0.21$ for LaAlO_3 and $\alpha/V_m = 0.215$ La_2O_3 while for the amorphous phase of $(\text{La}_{0.73}\text{Al}_{0.27})_2\text{O}_3$, using our k value, we obtain $\alpha/V_m = 0.19$. If we make the simplified assumption that the molar polarizability does not change with density between the crystalline and amorphous phases, then we can very approximately conclude from the ratio of the α/V_m values that the ratio of the densities, $\rho_{\text{amorph}}/\rho_{\text{crystalline}} \sim 0.9$. In simple terms, our experimental dielectric constant is consistent with the density of the amorphous phase of

$(\text{La}_{0.73}\text{Al}_{0.27})_2\text{O}_3$ being $\sim 90\%$ of the crystalline phase value for LaAlO_3 or La_2O_3 . Interestingly, if one uses a similar analysis for the case of amorphous and crystalline Al_2O_3 , then one also concludes that $\rho_{\text{amorph}}/\rho_{\text{crystalline}} \sim 0.9$.

One may also take into consideration the refractive index measurements using the well-known Lorentz–Lorenz equation:

$$(n^2-1)/(n^2+2) = (4\pi/3)\alpha_{\text{opt}}/V_m, \quad (3)$$

where α_{opt} is the optical frequency molecular polarizability. Assuming the measured value of the refractive index for our films is typically ~ 1.8 following annealing, then we deduce $\rho_{\text{amorph}}/\rho_{\text{crystalline}} \sim 0.87$ using the known¹³ refractive index for LaAlO_3 and an extrapolated value¹⁵ ~ 2.0 for La_2O_3 . This is sufficiently close to the value of the ratio determined from dielectric constant measurements given herein to give strong support to the hypothesis that amorphous $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ with $x > 0.5$ is approximately 10% less dense than its crystalline counterpart.

Several interesting scientific issues arise related to the network structure of amorphous $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ and the amorphous-to-crystalline phase transformation. In e-beam evaporated material we have found, as have other authors,⁶ that the amorphous phase is stable even after 700°C annealing. Similarly, the rf sputtered material we have studied here was also stable to high-temperature anneals. rf sputtered $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ deposited on substrates heated to 850°C was also found to remain amorphous if the O_2 pressure in the reactor was maintained higher than ~ 0.1 mTorr.¹⁶ It is clear from these results that the amorphous phase is very stable. Nuclear magnetic resonance measurements¹⁷ on $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ have evidenced the presence of AlO_4 , AlO_5 , and AlO_6 network units in numbers which depend upon both the relative concentrations of Al and La and the annealing temperature. In the amorphous stoichiometric (LaAlO_3) phase, it is found that substantial numbers of AlO_4 structures are present even at temperatures as high as 600°C . One is then tempted to ask whether the amorphous stability is related to this unusual bonding. Similar structures are found in the results of calculations¹⁸ of the network in Al_2O_3 , where it is suggested that the lower density of the amorphous network (as compared to the crystalline phase) may in part result from the presence of nominally undercoordinated Al's. In consequence, we suggest that the lower density of the amorphous $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ samples studied here as compared to the crystalline phases LaAlO_3 and La_2O_3 is due to a network coordination effect rather than, for example, the presence of porosity which might also be invoked in explaining reduced network density. This coordination effect may be due in part to the nonstoichiometry of our films (i.e., neither LaAlO_3 nor La_2O_3). It is clearly possible that stoichiometric phases would have better atomic packing leading to higher densities as in the case, for example, of most of the SiO_2 crystalline polymorphs when compared with amorphous SiO_2 . Measurements to confirm the coordination in the thin films would be valuable.

V. CONCLUSION

If the results presented here are confirmed, it would appear that amorphous $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ with $x > 0.5$ is less dense than its crystalline counterpart, and this results in a dielectric constant that is significantly reduced. The primary advantage of using this material is then lost since other Si compatible oxides with similar dielectric constants are available in the form of $\text{Hf}_x\text{Si}_y\text{O}_{2-z}\text{N}_z$. Furthermore, we have established that high-temperature annealing results in an interaction between the $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ and the underlying Si even though thermodynamics failed to predict this. On this basis, there would appear to be no salient feature which drives one to use $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ rather than other already available dielectrics.

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